Longitudinal growth, morphology and physical properties of fibrillar polyethylene crystals.

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SUMMARY

This thesis describes the longitudinal growth of fibrillar polyethylene crystals from flowing xylene solutions as well as the morphology and physical properties of the grown crystals.

Longitudinal growth of fibrillar polymer crystals is characterized by the fact that the growth front proceeds parallel to the chain direction, in contrast to the already extensively investigated growth of folded-chain lamellae that proceeds normal to the polymer chains (Chapter 1). Fibrillar crystal growth may be encountered in many biological and technological systems, especially in those where the macromolecules become deformed by flow. Moreover, this type of growth may lead to materials with very interesting mechanical properties.
However, the longitudinal growth process is still a relatively unexplored topic. Longitudinal growth rates for instance had not been reported before we began our study. Therefore, the investigations on the longitudinal growth as described in this thesis were started with the development of some new techniques for measuring the rates at which fibrillar crystals grow under well-defined conditions of flow for the model system linear polyethylene/p-xylene. Furthermore, the structure and morphology as well as the mechanical properties and the melting behaviour of the grown fibrillar polyethylene crystals were extensively investigated since the information provided by such studies reflects details of the mechanism underlying the longitudinal growth.

At first, growth measurements were carried out in laminar Poiseuille flow by placing fibrillar crystal seeds at the entrance of a capillary through which a supercooled polyethylene solution was allowed to flow (Chapter 2). Longitudinal growth rates were determined by winding the growing crystals on a roll with a speed

that was adjusted to the growth rate. Under such 'steady-state' conditions, fibrillar crystals with circular cross-sections in the range of 50 microns could continuously be produced at growth rates of the order of 1 cm/min.

A second, independent method for determining the growth rate was obtained by growing the seed crystals at a fixed position in the capillary. Under such 'static' conditions, tapered shaped crystals developed which allowed determination of the total length for a given period of time and thereby thus the growth rate. These growth rates agreed very well with the rates as determined by the steady-state method. The values varied between 0.01 and 2 cm/min and were found to increase with increasing flow rate, polymer concentration and degree of supercooling. This latter observation suggests that a nucleation step is involved in this longitudinal growth process for which a maximum crystallization temperature of 113 ^{o}C was found.

Scanning electron micrographs showed that the fibrillar crystals, also referred to as macrofibers, are composed of an aggregated bundle of striated elementary fibrils of the Shish-Kebab type. These structures may be visualized as 'backbones' of continuous extended-chain crystals with lateral dimensions of a few hundred Å (the Shish), overgrown by a large number of regularly spaced folded-chain lamellae at distances between 1000 and 2000 Å (the Kebab). Further morphological observations showed that the longitudinal growth was nucleated at the lateral surface of the seed crystals. It is believed that the growth of the macrofibers occurs by the simultaneous crystallization of a large number of 'backbones' by the action of the local flow field, thereby stipulating that the growth rates of all individual fibrils are the same.

Additional growth rate experiments were performed in simple shear flow as evoked by rotating the inner cylinder of a Couette-type apparatus (Chapter 3). Steady-state and static grow rate measurements yielded values similar to those obtained at corresponding local velocity gradients in the Poiseuille set-up, provided that the seed crystals were allowed to grow at some distance from the surface of the rotor (referred to as free-growth).

Under otherwise identical crystallization conditions however, a quite different growth process with much faster growth rates up to 50 cm/min was found when the growing crystals came in contact with the rotor surface. Under such conditions(referred to as surface-growth),large amounts of continuous fibrillar crystals with lengths of several kilometers could be produced and growth appeared to be possible up to temperatures of 120.5 ^{o}C which is well above the thermodynamic dissolution temperature of 118.6 ^{o}C for ideal polyethylene crystals in a dilute xylene solution. This surface-growth process was found to be promoted by both an increase in roughness and a decrease in polarity of the rotor surface. Moreover, growth rates could be changed reversibly within a broad range without changing the other crystallization parameters. Scanning electron micrographs reveal that these surface-growth fibers are again composed of bundles of elementary fibrils of the Shish-Kebab type although the macrofibers are now rectangular in cross-section. The various aspects of the surface-growth process point to the presence of a layer of adsorbed polymer molecules on the rotor surface that is capable of forming firm entanglements with the crystallizing molecules at the tips of the 'backbones' of the elementary fibrils, thereby deforming these molecules to such an extent that crystallization is strongly promoted.

Detailed morphological investigations by both scanning (SEM) and transmission (TEM) electron microscopy and by small-angle X-ray scattering (SAXS) reveal that the amount of lamellar overgrowth on the 'backbones' of the elementary fibrils decreases with increasing crystallization temperature and growth rate of the fibrillar crystals (Chapter 4). Elementary fibrils of surface-growth fibers crystallized above 114 ^{o}C at a sufficiently high speed are almost completely smooth.

The lateral dimensions of the elementary fibrils were acquired from dark-field images and line-broadening analysis of the (110) and (200) spots in the electron diffraction pattern in the TEM, as well as from analysis of continuously recorded equatorial wide-angle X-ray diffractograms (WAXD) and SAXS Guinier plots. The values as obtained from all these various techniques agreed remarkably well. These lateral dimensions were found to decrease

from about 260 Å for fibrillar crystals grown by the free-growth technique at 103 °C and a growth rate of 2 cm/min to approximately 150 Å for surface-growth fibers, crystallized at 118 °C at a rate of 12.6 cm/min.

WAXD diffractograms revealed the presence of a considerable amount of the triclinic crystal modification in the latter fibrillar crystals. This points again to the extensive coil deformation of the crystallizing molecules during the surface-growth process, especially at high temperatures and growth rates. As a result, the polymer chains 'unroll' to a much larger extent into the extended-chain backbones so that less chain material is left for the formation of the lamellar overgrowth at high temperatures and growth rates.

The mechanical properties of the surface-growth fibrillar crystals are quite remarkable and stress-strain diagrams of smooth high temperature fibers even reveal a Hookean behaviour (Chapter 5). Fibrillar crystals grown at 119.5 °C show an ultra-high Young's modulus of 100 x 10^4 kg/cm^2, and values of 29.5 x 10^3 kg/cm^2 and 3.6% for the tensile strength and elongation at break, respectively. This value for the Young's modulus exceeds the values for the moduli of glass fibers and steel and amounts to 45% of the theoretical value for ideal polyethylene crystals. Both the Young's modulus and the strength at break of the macrofibers showed a strong increase with increasing crystallization temperature. This behaviour may largely be attributed to the decrease in the amount of lamellar overgrowth.

The melting behaviour of the fibrillar crystals was mainly investigated by 'differential scanning calorimetry' (DSC) (Chapter 6). The DSC thermograms in general contain 3 melting endotherms around 140, 150 and 160 °C. All peaks were found to be strongly superheatable. Moreover, the sizes of the endothermic peaks decreased with increasing heating rate. Both effects illustrate the very slow randomization of the extended polymer chains in the fibrillar crystals to the random coil conformation during the melting process. This view is underlined by shrinkage measurements in silicone oil.

From the morphology of the fibrillar crystals as described in Chapter 4, it is concluded that the various melting endotherms

may not entirely be ascribed to the melting of distinct crystal morphologies. Their presence arises also from constraints to shrinkage during the melting process. Reduction of the fiber length of smooth fibrillar crystals by cutting to very short pieces or more particularly by selective etching with fuming nitric acid led to the complete disappearance of the two high temperature melting endotherms at 150 and 160 °C. Moreover, etching resulted in a complete absence of superheatability of the remaining peak at 136 °C and increased the heat of fusion up to 70 cal/g. On melting longer fibers,the melting endotherms at 150 and 160 °C show up, and constrained fibrillar crystals reveal in fact only these two high temperature endotherms.

Wide-angle X-ray diffractograms, taken on a constrained macrofiber while gradually heated, show that the normal orthorhombic crystal form transforms around 150 °C into the liquid crystalline hexagonal modification. Retractive force measurements in a dynamometer by heating bundles of fibrillar crystals at constant length show a maximum at this temperature beyond which the stress decays.

From all these observations it is inferred that the first melting endotherm in the DSC thermograms arises from the melting of unconstrained fibrillar crystal parts which are able to shrink during this fusion process. Moreover, the melting of the lamellar overgrowth on the elementary fibrils may contribute to this endotherm. The second melting endotherm is associated with the transformation of the orthorhombic into the hexagonal lattice in constrained sample parts and the third endotherm arises from the melting of this latter crystal modification. The melting of this hexagonal or 'rotator' phase is accompanied by slippage of the polymer chains past each other and randomization of the chains to the higher energy gauche states. Fully constrained smooth high temperature grown fibrillar crystals absorb a heat of over 15.5 cal/g during this process, indicating that the polymer chains in such fibers should be highly extended.

Strained fibrillar crystals reveal a complex relaxation behaviour, presumably due to the presence of 'kink bands'. Scanning electron micrographs and visual observations of the melting process under the optical microscope confirm the presence of these macroscopic

defect regions.

Finally, the influence of the crystallization conditions of the fibrillar crystals on the melting behaviour was investigated. DSC thermograms show a strong increase in both the heat of fusion and the temperature positions of the endothermic peaks with increasing crystallization temperature. In addition, the dynamometer curves reveal with increasing temperature a strong increase in the maximum retractive force. Both effects reflect the decrease in the amount of lamellar overgrowth in the fibrillar crystals when grown at higher temperatures.